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**The Rate of Volcanism on Venus**

by

Bruce Fegley, Jr. and Ronald G. Prinn

Department of Earth, Atmospheric, and Planetary Sciences  
Massachusetts Institute of Technology  
Cambridge, MA 02139 USA

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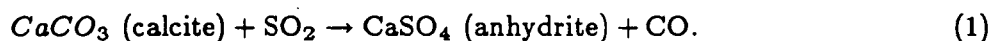
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The maintenance of the global  $H_2SO_4$  clouds on Venus requires volcanism to replenish the atmospheric  $SO_2$  which is continually being removed from the atmosphere by reaction with calcium minerals on the surface of Venus.<sup>1-4</sup> The first laboratory measurements of the rate of one such reaction, between  $SO_2$  and calcite ( $CaCO_3$ ) to form anhydrite ( $CaSO_4$ ), are reported here. If the rate of this reaction is representative of the  $SO_2$  reaction rate at the Venus surface, then we estimate that all  $SO_2$  in the Venus atmosphere (and thus the  $H_2SO_4$  clouds) will be removed in 1.9 million years unless the lost  $SO_2$  is replenished by volcanism. The required rate of volcanism ranges from about 0.4 to about 11 km<sup>3</sup> of magma erupted per year, depending on the assumed sulfur content of the erupted material. If this material has the same composition as the Venus surface at the Venera 13, 14 and Vega 2 landing sites<sup>5,6</sup> then the required rate of volcanism is about 1 km<sup>3</sup> per year. This independent geochemically estimated rate can be used to determine if either (or neither) of the two discordant (2 km<sup>3</sup> yr<sup>-1</sup> vs. 200-300 km<sup>3</sup> yr<sup>-1</sup>) geophysically estimated rates<sup>7-9</sup> is correct. The geochemically estimated rate also suggests that Venus is less volcanically active than the Earth.

The experiments utilized calcite, which is a net sink for  $SO_2$  by incorporating it into the Venus crust via the net reaction<sup>1-4</sup>



Calcite is also predicted by several authors to be present on the Venus surface because it appears capable of buffering the  $CO_2$  abundance on Venus via the Urey reaction ( $CaCO_3 + SiO_2 = CaSiO_3 + CO_2$ ).<sup>10-13</sup> These predictions concerning possible roles for calcite on Venus, the exemplary nature of reaction (1), and the availability of high purity  $CaCO_3$  in several forms led us to study reaction (1) as a paradigm for  $SO_2$  removal. However, as Figure 1 illustrates,  $SO_2$  also reacts with other calcium minerals (e.g., diopside  $CaMgSi_2O_6$ ), which are believed to be present on the surface of Venus.<sup>14,15</sup> The kinetics for these alternative reactions are also being measured and will be reported later.

Reaction (1) was studied by heating clear calcite crystals (Iceland spar) of known impurity

content ( $\sim 350$  ppm total impurities by inductively coupled plasma emission spectroscopy), weight, and surface area in  $SO_2$ -bearing gas streams for varying time periods at three different temperatures. Experiments were done at temperatures of 600-850°C and ambient atmospheric pressures with analyzed  $SO_2 - CO_2$  gas mixtures nominally containing 1% (by volume)  $SO_2$ . Thus, the  $SO_2$  molecular number density is about the same as at the surface of Venus where the atmospheric pressure is about 100 times larger but the  $SO_2$  volume mixing ratio is about 100 times smaller.<sup>16</sup> The mixtures also typically contained  $< 1$  ppm  $O_2$  and  $\leq 10$  ppm  $H_2O$  as impurities. Standard techniques were used to monitor and control gas flow and temperature (to better than  $\pm 5^\circ C$ ). The rate of reaction (1) was determined by three independent methods: (a) measuring the weight gain at the end of reaction, (b) using scanning electron microscopy (SEM) to measure the porosity and thickness of the reacted surface layers from micrographs of external and fracture surfaces (e.g., Fig. 1), and (c)  $SO_4^{2-}$  analyses of reacted samples by ion chromatography. SEM examination of many samples (in combination with X-ray line scans and energy dispersive spectroscopy (EDS) on the SEM) showed that  $CaSO_4$  layers covered all external surfaces of the reacted samples. X-ray powder patterns of samples and standards confirmed that the layers are anhydrite (in particular, there is no evidence for calcium sulfite) and that unreacted calcite is the only other phase present in the samples. The ion chromatography also verified the absence of anion impurities at levels  $\geq 10$  ppm.

The experimental run conditions and rate data are summarized in Table 1 and Figure 2. Rate data using the weight gain, SEM and  $SO_4^{2-}$  analysis methods for the same sample agree within the combined experimental uncertainties ( $1 \sigma$ ) shown in Table 1. A weighted linear least squares fit to the data gave the equation for the rate  $R = 10^{19.64(\pm 0.28)} \exp(-15,248 (\pm 2970)/T)$  molecules  $cm^{-2} s^{-1}$ . The corresponding activation energy is  $126.8 \pm 5.4$  kJ/mole. The rate of reaction (1) was extrapolated downward to Venus surface temperatures ( $\sim 660$ -750 K) using this equation and the Pioneer Venus radar altimetry data<sup>17</sup> and atmospheric (P, T) profile<sup>18</sup> to take the altitude dependence of the rate into account. The derived global mean  $SO_2$  reaction rate is  $\sim 4.6 \times 10^{10}$  molecules  $cm^{-2} s^{-1}$ .

Chemical analyses of the Venus surface by the Venera 13, 14 and Vega 2 spacecraft<sup>5,6</sup> give a  $CaO$  content (by mass) of 7.90% (weighted mean). Assuming the experimental rate is repre-

sentative of the  $SO_2$  depletion rate via reaction with calcium minerals on the Venus surface, the observed  $SO_2$  column density ( $2.2 \times 10^{23}$  molecules  $cm^{-2}$ )<sup>16</sup> would be removed from the Venus atmosphere in  $\sim 1.9 \times 10^6$  years in the absence of a comparable sulfur source. However, maintenance of the global  $H_2SO_4$  clouds, which are formed by the UV sunlight powered conversion of  $SO_2$  into  $H_2SO_4$  cloud particles,<sup>19</sup> requires a comparable sulfur source. This source must be endogenic because infalling cosmic material cannot supply enough sulfur. The calculated  $SO_2$  removal rate on Venus is equivalent to  $\sim 2.8 \times 10^{13}$  grams sulfur per year. However, the measured terrestrial flux of infalling material, which is roughly applicable to Venus because of similar sizes and masses, is only  $\sim 7.8 \times 10^{10}$  grams per year,<sup>20</sup> or only  $\sim 4.6 \times 10^9$  grams sulfur per year assuming the most sulfur-rich C1 chondrite composition.<sup>21</sup>

The most plausible endogenic source is volcanism, which has occurred on Venus in the past,<sup>22</sup> and which may have led to increased  $SO_2$  levels above the Venus cloud tops observed by the PV orbiter.<sup>23,24</sup> The rate of volcanism required to balance  $SO_2$  depletion via reactions with calcium minerals on the Venus surface depends on the sulfur content of the erupted material (gas and magma). If this material has an overall  $S/Si$  mass ratio of 0.03, the weighted mean of the Venera 13, 14, and Vega 2 surface analyses,<sup>5,6</sup> the corresponding rate of volcanism is  $\sim 1 \text{ km}^3 \text{ yr}^{-1}$ . Figure 3 illustrates that this rate is about 20 times smaller than the terrestrial value. Two other plausible models for the  $S/Si$  ratio of the erupted material on Venus are also shown: (a)  $S/Si \sim 0.1$ , as in ordinary chondrites,<sup>21</sup> giving a rate of  $\sim 0.4 \text{ km}^3 \text{ yr}^{-1}$ , and (b)  $S/Si \sim 0.004$  as in the Earth's crust,<sup>25</sup> giving a rate of  $\sim 11 \text{ km}^3 \text{ yr}^{-1}$ . All rates will scale as  $\epsilon^{-1}$ , where  $\epsilon$  is the S degassing efficiency for erupted material ( $0 < \epsilon \leq 1$ ). However  $\epsilon$  is likely to be close to unity because S gases are expelled directly into the atmosphere and hot, reactive S-bearing magmas will rapidly lose S to the atmosphere. Our experiments on a possible magma S-bearing mineral pyrite  $FeS_2$  being chemically weathered by  $CO_2$  indicate complete S loss in hours at sub-magmatic temperatures ( $\sim 980^\circ\text{C}$ ).

Figure 3 also illustrates that widely discordant volcanism rates have been estimated by two different geophysical methods: (a) rates of  $\sim 200\text{-}300 \text{ km}^3 \text{ yr}^{-1}$  by scaling terrestrial heat production to Venus and transporting the outward heat flux solely by volcanism<sup>8,9</sup> and (b) an upper limit of  $2 \text{ km}^3 \text{ yr}^{-1}$  by analysis of impact crater areal densities on Venera 15, 16 radar images<sup>7</sup>.

The present geochemically derived volcanism rate is independent of these two methods and in principal can be used to test if either (or neither) is correct. In particular, the values computed by geophysical method (a) do not agree with our geochemical values. Finally, this work also suggests that on average Venus is less volcanically active than the Earth.

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TABLE 1

Rate Data Used to Calculate the Activation Energy

<u>Sample</u>	<u>T(°C)<sup>a</sup></u>	<u>Duration (Hours)</u>	<u>Rate × 10<sup>-12</sup> (molecules cm<sup>-2</sup> s<sup>-1</sup>)<sup>b</sup></u>
R44-1	602	95	1.67 ± 0.19 <sup>c</sup>
R45-1	602	314	0.85 ± 0.77
			1.05 ± 0.12 <sup>c</sup>
R45-3	602	314	1.01 ± 0.11 <sup>c</sup>
R45-4	602	314	1.20 ± 0.51
			0.68 ± 0.48 <sup>d</sup>
R36-1	746	96	8.43 ± 2.93
			13.6 ± 6.0 <sup>d</sup>
R36-2	746	96	23.2 ± 6.2
			19.9 ± 11.0 <sup>d</sup>
R50-1	747	192	9.19 ± 1.60
R50-3	747	192	10.5 ± 7.8
R51-1	748	96	13.2 ± 4.0
R51-2	748	96	10.3 ± 5.6
R43-1	848	91	60.4 ± 6.8
			57.1 ± 31.7 <sup>d</sup>
R43-2	848	91	53.2 ± 7.0
			67.2 ± 43.4 <sup>d</sup>
R43-3	848	91	58.1 ± 7.0
			48.4 ± 12.1 <sup>d</sup>

Notes to Table 1<sup>a</sup> The estimated temperature uncertainty is ± 5°C.<sup>b</sup> The number of SO<sub>2</sub> molecules reacted per cm<sup>2</sup> surface area per second. The rate is from weight gain measurements unless noted otherwise. The 1  $\sigma$  uncertainties are also listed.<sup>c</sup> The rate from ion chromatography analyses of SO<sub>4</sub><sup>2-</sup> content of reacted sample.<sup>d</sup> The rate from scanning electron microscope (SEM) measurements of anhydrite layer thickness and porosity.



### Figure Captions

Figure 1. Scanning electron micrographs of chemically reacted samples. a, Fracture surface showing a  $\text{CaSO}_4$  (anhydrite) layer (A) completely covering a partially reacted calcite crystal (C) (850°C for 192 hours) b, Top surface showing  $\text{CaSO}_4$  (A) growing on a partially reacted diopside crystal (D) (833°C for 48 hours).

Figure 2. Arrhenius plot of rate data from Table 1 vs.  $1/T$ . The line is a weighted linear least squares fit. Rates determined from independent methods (wt. gain, SEM,  $\text{SO}_4^{2-}$  analyses) for the same sample agree within the  $1\sigma$  experimental uncertainties.

Figure 3. Geochemical and geophysical estimates of the rate of volcanism on Venus are compared to the terrestrial rate. Three plausible models for the  $S/S_i$  ratio of erupted material on Venus yield rates of  $\sim 0.4$  to  $\sim 11 \text{ km}^3 \text{ yr}^{-1}$ . Adopting the Venus surface  $S/S_i$  ratio from Venera 13, 14, and Vega 2 analyses<sup>5,6</sup> yields a rate of  $\sim 1 \text{ km}^3 \text{ yr}^{-1}$ , or about 20 times less than the rate of volcanism on Earth.

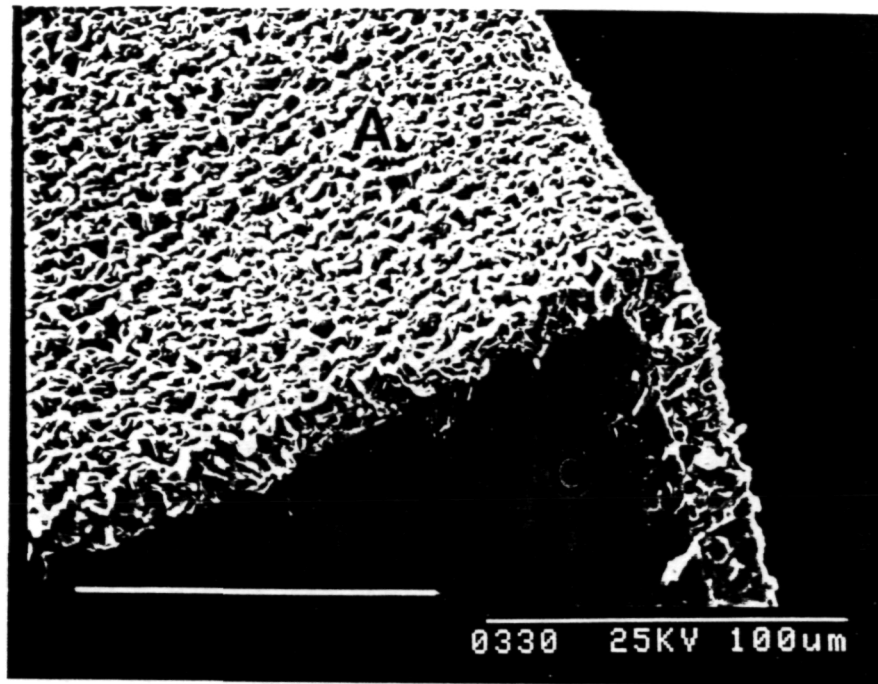


Figure 1A ORIGINAL PAGE IS  
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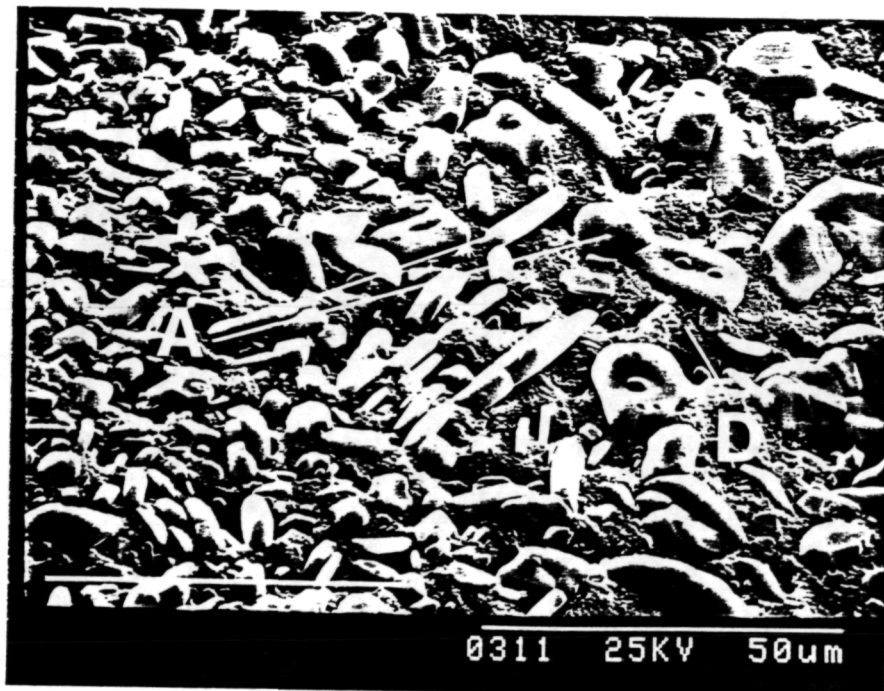


Figure 1B

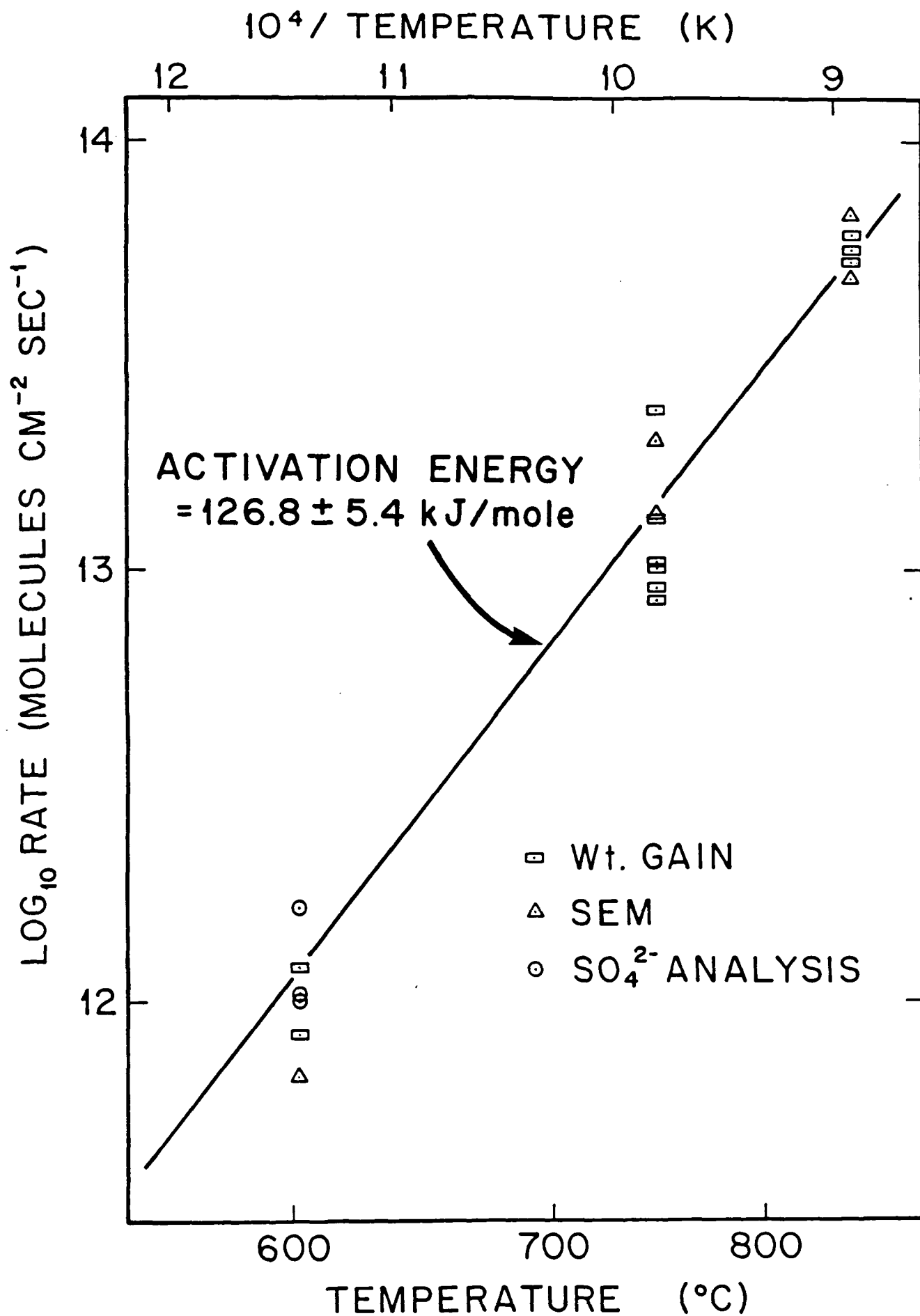


Figure 2

# VOLCANISM RATES

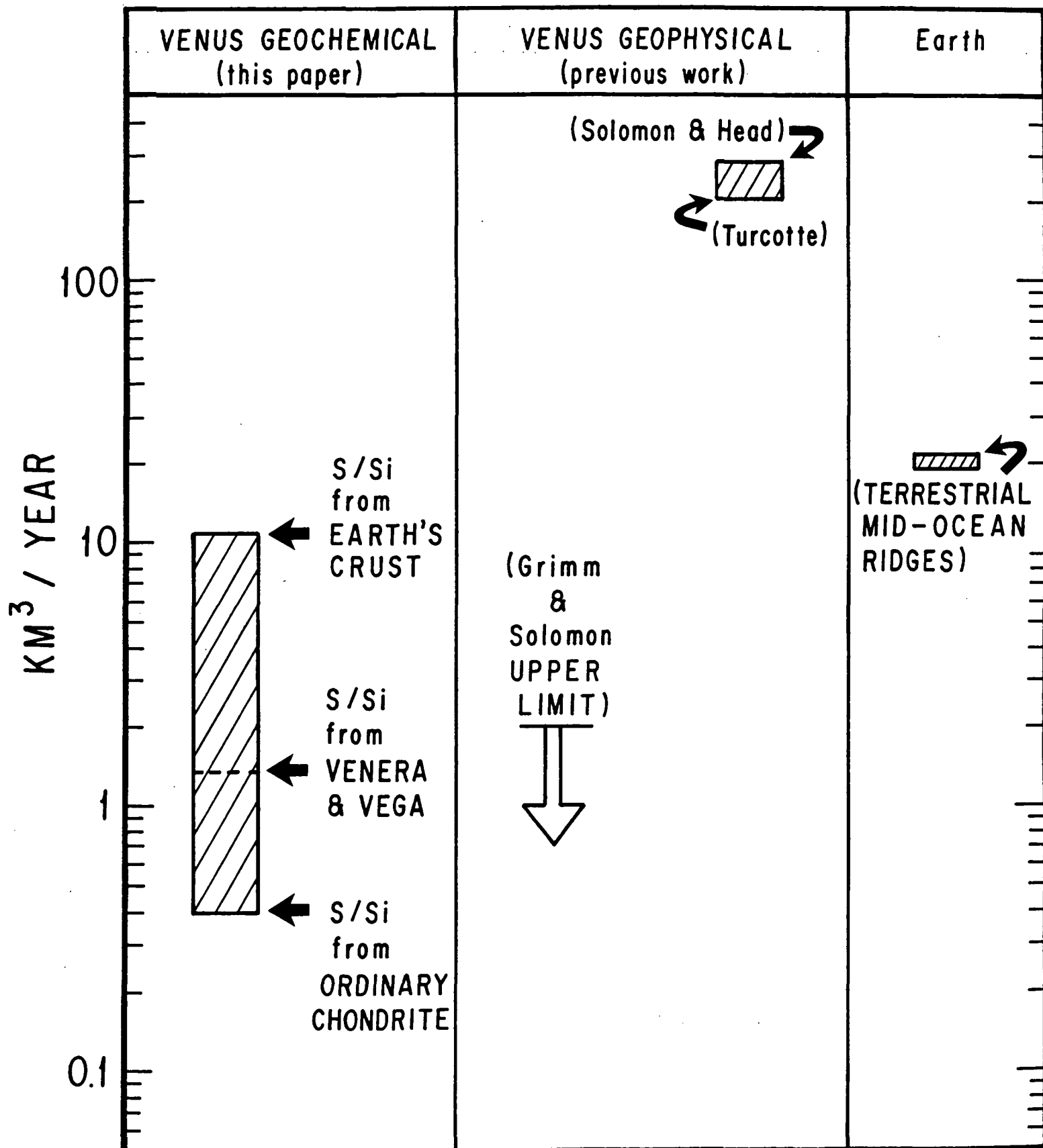


Figure 3